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Organometallic NLO Polymers. Accordion Main-Chain NLO Polymers of Ferrocene

by

Michael E. Wright and Matthew S. Sigman

Department of Chemistry & Biochemistry, Utah State University, Logan, Utah 84322-0300

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Bis(ferrocene) NLO-phore monomers were prepared. The new *bis*(ferrocene) monomer was successfully copolymerized with *bis*(cyanoacetate) comonomers using a Knoevenagel polycondensation technique. The polymers were characterized by spectroscopic, thermal analysis, and GPC data. The polymers had average molecular weights in the range of 5000 to 25,000.

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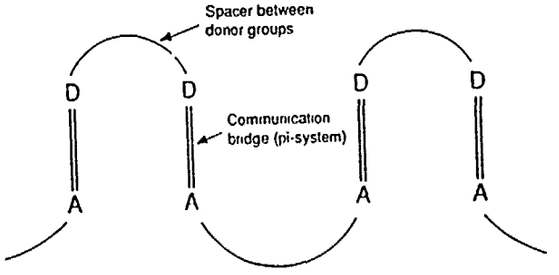
ORGANOMETALLIC NLO POLYMERS. ACCORDION MAIN-CHAIN NLO POLYMERS OF FERROCENE

Michael E. Wright* and Matthew S. Sigman

Department of Chemistry & Biochemistry,
Utah State University, Logan, Utah 84322-0300

Introduction

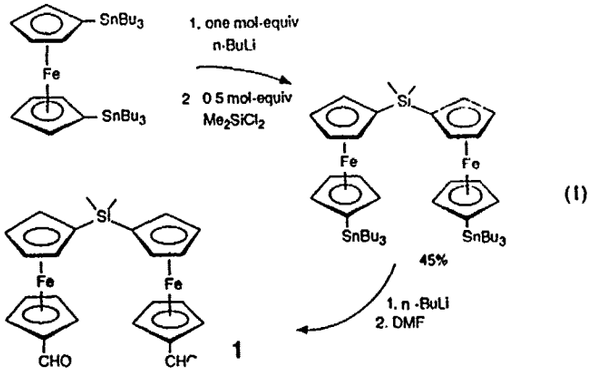
In the previous paper[1] we presented the synthesis of linear organometallic main-chain NLO polymers. Our research has continued to focus on ferrocene based NLO polymers because of the outstanding results obtained by Marder and coworkers using crystalline ferrocene complexes.[2] The ability to selectively functionalize the cyclopentadienyl rings of ferrocene has given us the ability to prepare elaborate organometallic NLO-phores.[1,3] Lindsay and coworkers recently presented the synthesis of a new class of main-chain organic NLO polymers.[4] For this new class of NLO polymers, the aligning process need not reorient the entire polymer chain, but rather, only fold the polymer backbone into the accordion shape.



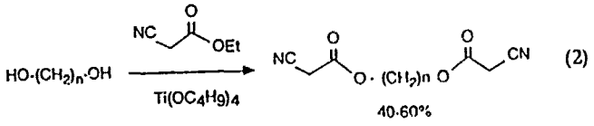
In this paper we present the synthesis and characterization of organometallic polymers with the potential of adopting the accordion macrostructure. As we saw in the previous paper, the use of the Knoevenagel condensation appears to be the most effective manner to prepare polymers of good molecular weight and tractability.

Results & Discussion

Monomer Synthesis & Characterization. Selective mono-transmetalation of the ferrocene complex $\{\eta^5\text{-}C_5H_4SnBu_3\}_2Fe$[4] followed by reaction with one-half mol-equiv of dimethyldichlorosilane afforded the bridged ferrocene system in 45% isolated yield (eq 1). Separation of $\{(\eta^5\text{-}C_5H_4SnBu_3)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ from $SnBu_4$, which is also a product in the reaction, proves to be very difficult. The separation is made even more difficult by the necessity to deactivate the alumina column by treatment with ether prior to use. It turns out the most efficient route to 1 is to use the *bis*-ferrocenyl compound contaminated with $SnBu_4$ (~10 mol-%, the exact ratio was determined in ^1H NMR spectra). The $SnBu_4$ does not appear to have any deleterious effects on the yield in the final transmetalation step. Monomer 1 is isolated in a 30% overall yield starting from $\{\eta^5\text{-}C_5H_4SnBu_3\}_2Fe$.

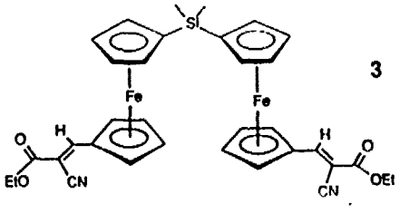


The *bis*(cyanoacetate) monomers 2 were prepared by reaction of the appropriate diol with an excess of ethyl cyanoacetate in the presence of a catalytic amount of $Ti(OC_4H_9)_4$ (eq 2).[7] At the completion of the reaction the monomers are purified by crystallization from ethyl acetate/hexanes. Monomers 2a-c are white crystalline materials which can be stored at ambient temperature for months without decomposition.



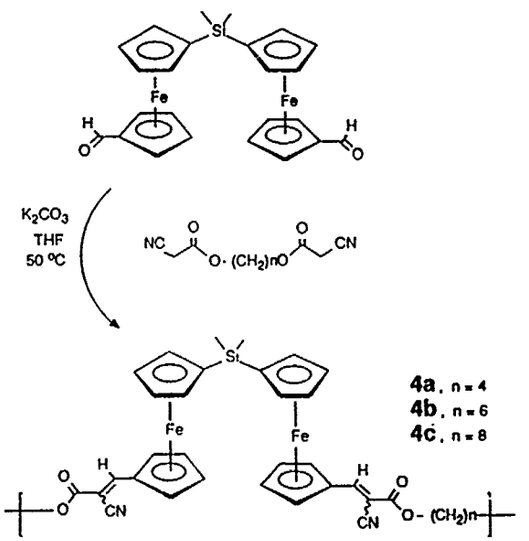
2a, n = 4
2b, n = 6
2c, n = 8

Copolymer Synthesis & Characterization. Our initial strategy to prepare the accordion copolymers was to carry out a polycondensation of monomer 3 with various diols. This method appeared highly desirable because it has proven very successful for main-chain organic NLO polymers prepared thus far. Monomer 3 is treated with hexanediol in the presence of $Ti(OC_4H_9)_4$ (2 mol-%) at 150 °C for 16 h. The product of the reaction is found to be intractable in all solvents. Elemental analysis data is close to that anticipated for the polymeric product; however, the lack of solubility is not consistent with other results we will present later.



The results above suggest that the reaction conditions required to carry out the Lewis acid catalyzed transesterification polycondensation are having deleterious effects on the ferrocene monomer and/or the polymeric product. It is at this point we changed our strategy and decided to construct the polymer backbone through the Knoevenagel condensation reaction. For the ferrocenecarboxaldehydes we find this reaction to proceed in very high yields and can be accomplished using very mild reaction temperatures (25 - 50 °C). This reaction also possesses good functional group tolerance because of the mild base (*i.e.* K_2CO_3 or DMAP) used. This latter point will become important in future generations of NLO polymers being prepared in our laboratory.

Scheme 1



The copolymerization of monomers 1 and 2 is carried out by heating a THF solution to 50 °C in the presence of excess potassium carbonate for 12 h (Scheme 1). Spectroscopic analysis of the crude polymer indicates a mixture of *E*- and *Z*-isomers are formed in the polymerization reaction. The *E*/*Z* ratio is found to vary in the range of 5 to 10. When the copolymers are purified by precipitation into methanol the *E*-isomer is enriched to ~95%. Evidently the copolymer which contains ratio of *Z*-isomers exhibits higher solubility.

The accordion main-chain organometallic polymers are soluble in most organic solvents (*e.g.* benzene, chloroform, dichloromethane, and tetrahydrofuran) and for **4c** we are able to cast free-standing films. Gel permeation chromatography of the polymers show that comonomer **2c** afforded the highest molecular weight polymer (M_n = 25,000). Films of polymer **4c** are elastic and can be stretched by nearly 100% of their original length before tearing. The lower molecular polymers form films which are much more brittle.

Concluding Remarks

In this study we have demonstrated the feasibility of preparing accordion organometallic NLO polymers. The key to our success in obtaining the novel polymers was the utilization of a Knoevenagel polycondensation technique. The mild reactions conditions overted deleterious reactions which we seem to incurr when heating ferrocenyl NLO-phore monomers in the presence of Lewis acids.

Experimental Section

Preparation of Copolymer **4**. A solution of THF (4 mL) containing $\{(\eta^5\text{-}C_5H_4CHO)Fe(\eta^5\text{-}C_5H_4)\}_2SiMe_2$ (0.200 g, 0.413 mmol), $CNCH_2CO_2(CH_2)_6O_2CCH_2CN$ (0.104 g, 0.413 mmol), and K_2CO_3 (0.35 g, 0.62 mmol) was heated at 50 °C for period of 12 h. The mixture was filtered through Celite and the solvents removed under reduced pressure. The crude product was dissolved in chloroform and precipitated in methanol. The copolymer was collected and washed with cold methanol (3 x 25 mL) and then dried under reduced pressure at 65 °C for 24 h.

Copolymer **4c**. ^1H ($CDCl_3$) δ 8.08 (s, 2 H), 4.92 (t, *J* = 1.9 Hz, 4 H), 4.59 (t, *J* = 1.9 Hz, 4 H), 4.49 (t, *J* = 1.7 Hz, 4 H), 4.25 (t, *J* = 6.5 Hz, 4 H), 4.14 (t, *J* = 1.7 Hz, 4 H), 1.72 (m, 4 H), 1.39 (m, 8 H), 0.49 (s, 6 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 163.1 ($\underline{C}O_2$), 158.3 (=CH), 116.7 (CN), 97.6 (=$\underline{C}$(CN)), 75.1 (Cp CH), 74.2 (Cp CH), 74.16 (*ipso*-Cp CH), 73.9 (Cp CH), 73.5 (*ipso*-Cp), 71.8 (Cp CH), 66.1 (OCH_2), 29.0, 28.4, 25.7 (CH_2's), -1.4 ($SiCH_3$). IR (CH_2Cl_2) ν_{CN} 2222, $\nu_{C=O}$ 1718, and $\nu_{C=C}$ 1593 cm^{-1}. Anal. Calcd for $\{C_{38}H_{46}Fe_2N_2O_4Si\}_n$: C, 62.05; H, 5.53; N, 3.84%. Found: C, 61.70; H, 5.44; N, 3.76%.

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References and Notes

1. For part 2 in the series see: Wright, M. E.; Toplikar, E. G. *Polym. Prepts*, preceeding paper in this issue.
2. Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Schaefer, W. P. *Organometallics* **1991**, *10*, 1896 and references cited therein.
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4. Lindsay, G. A.; Fischer, J. W.; Henry, R. A.; Hoover, J. M.; Kubin, R. F.; Seltzer, M. D.; Stenger-Smith, J. D. *Polym. Preprints* **1991**, *32(2)*, 91.